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DIELS-ALDER REACTION OF HEXAKIS(TRIFLUOROMETHYL)BENZVALENE

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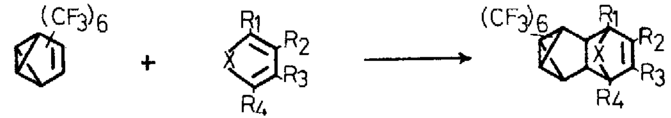
In the investigation of the reactivity of hexakis(trifluoromethyl)benzvalene (I), reaction of I with butadiene was found to give a Diels-Alder adduct.1)

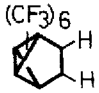
In this study, general applicability of this reaction and stereochemistry of the adduct are reported. Reaction of I with some dienes are summarized in Table I. Analyses of spectral data show that these products are Diels-Alder adducts except in the case of cyclohexadiene, but these analyses could not tell the stereochemistry of the adducts. Haszeldine et al. recently reported that the reaction of I with pyrrole2) and cyclopentadiene3) gave Diels-Alder adducts, but they did not determine the stereochemistry (endo or exo) of the products. From the results shown in Table I, it is assumed that the reaction proceeds through the exo-form in the transition state: (1) methyl group on the terminal carbon of butadiene markedly decreased in the reaction rate, while those on the middle carbons rather increased, (2) pyrrole gave the adduct, but N-methylpyrrole was completely recovered, and (3) cyclopentadiene gave the adduct, but cyclohexa-1,3-diene gave other products. To ascertain these assumptions, an X-ray analysis was carried out on the dibromide of the adduct of I with furan. The structure was determined as exo-form, as shown below.

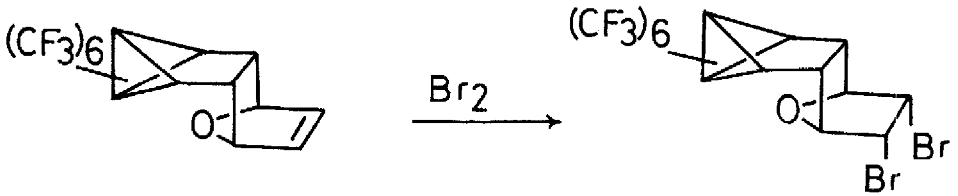
Table I.



group	-X-	R_1	R_2	R_3	R_4	T°	time	solvent	yield(%)
butadienes	-H,H-	H	H	H	H	90	4 hr	n-C_5H_{12}	quant.[1]
		CH_3	H	H	H*)	100	18 hr	$(CH_3)_2CO$	85.9
		CH_3	H	H	CH_3			no reaction	
		H	CH_3	H	H	RT	20 days	$(CH_3)_2CO$	43.0
		H	CH_3	CH_3	H	RT	10 hr	n-C_5H_{12}	52.3
furans	-O-	H	H	H	H	RT	5 min	n-C_5H_{12}	quant.
		CH_3	H	H	CH_3	RT	8 days	n-C_5H_{12}-$CHCl_3$	91.7
		CH_3	CH_3	CH_3	CH_3	RT	8 days	n-C_5H_{12}-$CHCl_3$	66.7
pyrroles	-N- H	H	H	H	H	RT	6 months	n-$C_5H_{12}CHCl_3$	11.8
	-N- CH_3	H	H	H	H			no reaction	
cycloalkanes	-CH_2-	H	H	H	H	RT	5 min	n-C_5H_{12}	quant.
	-CH_2-CH_2-	H	H	H	H	90	7 days	CCl_4	**)

*) trans-1,3-pentadiene

**)  and  were obtained in 75% and 80%, respectively.



The crystal sealed in a thin-walled glass capillary was mounted on a Rigaku computer-controlled four-circle diffractometer and measured with Cu Kα radiation from a graphite monochrometer.

Crystal data: 2,3,4,5,6,7-hexakis(trifluoromethyl)-9,10-dibromo-11-oxa-pentacyclo[6.2.1.0.^{2,7}0.^{3,5}0^{4,6}]undecane $C_{16}H_4OBr_2F_{18}$; M.W. 714; mp 109°; Cell dimensions, a = 15.092, b = 15.128, c = 9.157 Å, V = 2090.7 Å^3; Space group, $P2_12_12_1$; Z, 4; D calc. 2.276 g/cm^3.

Table II. Atomic Coordinates*

Atom	x	y	z	Atom	x	y	z
Br 1	.4118 (3)	.0356 (3)	.7105 (9)	F 13	.359 (2)	.324 (2)	.545 (4)
Br 2	.2157 (3)	.0579 (2)	.7106 (5)	F 14	.221 (2)	.364 (2)	.488 (5)
C 1	.314 (2)	.106 (2)	.641 (4)	F 15	.281 (2)	.245 (2)	.423 (3)
C 2	.216 (2)	.062 (2)	.637 (3)	F 17	.130 (2)	.172 (1)	.436 (2)
C 3	.163 (3)	.121 (2)	.753 (4)	F 18	.058 (2)	.290 (1)	.503 (3)
C 5	.302 (2)	.182 (2)	.757 (4)	F 19	.019 (1)	.154 (1)	.555 (4)
C 6	.240 (2)	.260 (2)	.681 (3)	F 21	-.020 (2)	.299 (1)	.945 (4)
C 7	.141 (2)	.216 (2)	.693 (3)	F 22	-.010 (2)	.176 (1)	.874 (3)
C 8	.096 (2)	.272 (2)	.795 (5)	F 23	-.053 (1)	.276 (1)	.746 (3)
C 9	.134 (2)	.366 (2)	.803 (4)	F 25	.379 (1)	.351 (1)	.858 (3)
C 10	.224 (2)	.339 (2)	.804 (4)	F 26	.275 (2)	.440 (2)	.957 (3)
C 11	.160 (5)	.306 (2)	.909 (4)	F 27	.315 (2)	.455 (1)	.748 (3)
C 12	.279 (3)	.307 (2)	.543 (4)	F 29	.020 (3)	.468 (2)	.862 (4)
C 16	.084 (3)	.193 (3)	.536 (7)	F 30	.040 (3)	.459 (1)	.687 (5)
C 20	.007 (3)	.259 (2)	.834 (6)	F 31	.141 (2)	.516 (1)	.793 (4)
C 24	.291 (3)	.392 (2)	.838 (5)	F 33	.115 (3)	.219 (1)	1.114 (3)
C 28	.088 (2)	.451 (2)	.791 (4)	F 34	.139 (3)	.359 (1)	1.144 (2)
C 32	.156 (5)	.293 (5)	1.093 (6)	F 35	.256 (3)	.287 (2)	1.111 (2)
O 4	.235 (2)	.145 (1)	.850 (2)				

*The standard deviations are shown in parentheses denoting the least significant digits in atomic coordinates.

The three-dimensional intensity data were collected with the θ-2θ scan technique at a constant scanning rate of 4° 2θ/min. Three standard reflections were measured after every 52 reflections. The sum of the F_o values of the three reflections was used to scale the observed intensity. The maximum deviation of the sums from their mean value was 2.9%. A total of 1947 reflections were obtained as observed in the range of $2\theta \leqq 135°$. The intensity data were then corrected for Lorentz and polarization factors but not for absorption and extinction factors. The structure was solved by the heavy atom method. Refinement of the positional and the thermal parameters of the non-hydrogen atoms was carried out by the block-diagonal least-squares method, in which the anisotropic thermal vibrations were assigned. Five cycles of the refinement gave the R-value of 0.155. Oxygen and fluorine atoms were distinguished by the chemical consideration. At this stage, difference Fourier synthesis was carried out using the parameters obtained from the above refinement, but no other atoms could be found. The weighting system adopted in the least-squares refinement is 1.0 for all observed reflections. The final atomic parameters are listed in Table II with their estimated standard deviations in parentheses. Fig. 1 shows the conformation and bond lengths of the molecule.

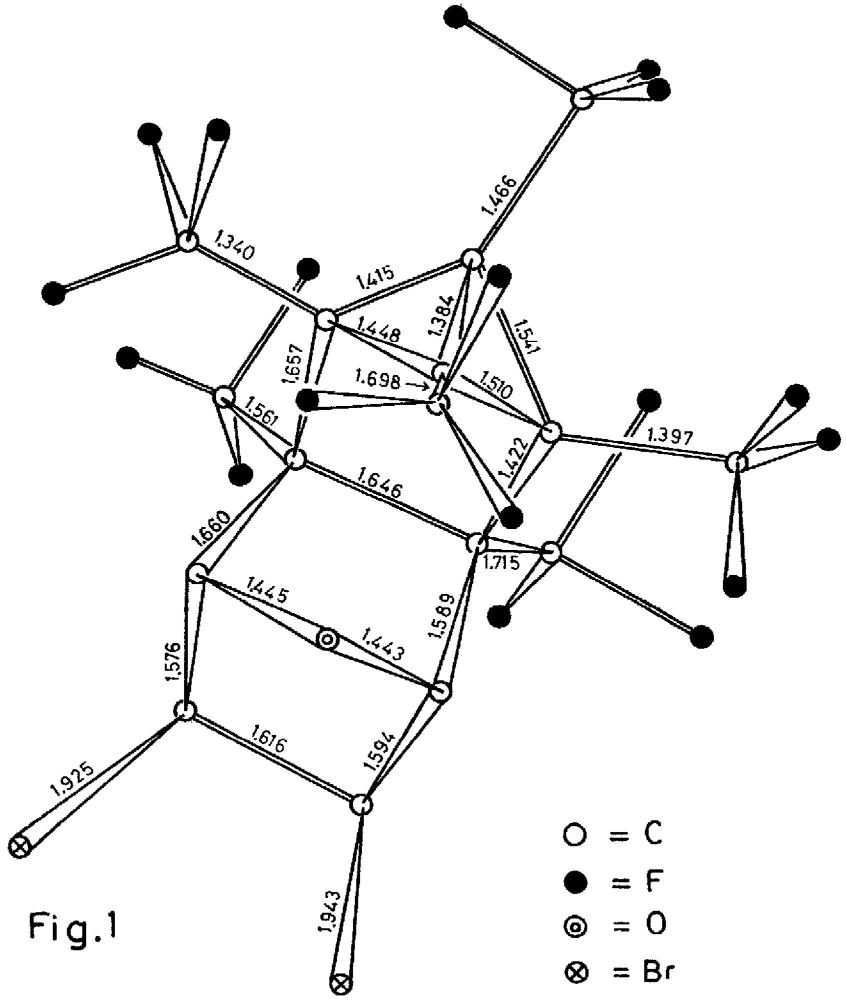


Fig.1

The average length of the 18 C-F bonds is 1.307Å. The mean standard deviation of the C-C bond lengths is estimated to be 0.046Å and that of the C-F bonds is 0.054Å.

This result shows the Diels-Alder reaction of I passes through the exo-form, rather than the endo-form, which is considered to be more favorable in many Diels-Alder reactions; namely, trifluoromethylated bicyclobutane part of I might prevent the diene from approaching in the endo-form.

References

1) Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Hanzawa, and M. Honda, Tetrahedron Letters, 1975, 3819.
2) M.G. Barlow, G.M. Harrison, R.N. Haszeldine, R. Hubbard, M.J. Kershaw, and D.R. Woodward, J. Chem. Soc., Perkin I, 1975, 2010.
3) M.G. Barlow, R.N. Haszeldine, and R. Hubbard, J. Chem. Soc.(c), 1970, 1232.